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ZnO:HCl single crystals: Thermodynamic analysis of CVT system, feature of growth and characterization

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ABSTRACT

The full thermodynamic analysis of using HCl as a chemical vapor transport (CVT) agent (TA) for ZnO single crystals growth in closed growth chambers, including 16 chemical species, is carried out for wide temperature and loaded TA pressure ranges. The influence of the growth temperature, of the TA density and of the undercooling on the rate of ZnO mass transport was investigated theoretically and experimentally. It is shown that the mass transport is diffusion-limited at about 1050 °C, and it is limited by kinetics of the CVT reaction at lower temperatures. It is experimentally shown that using HCl favors obtaining void-free n-ZnO crystals with controllable electrical parameters, it reduces the effect of adhesiveness to the walls of the growth chamber. The characterization by the photoluminescence spectra, the transmission spectra and the electrical properties in the wide temperature range allowed analyzing energy spectra of Cl-containing stable defects in ZnO and electrical activity of Cl donors. Some methods of activation energy correction for Cl-containing centers are discussed.

1. Introduction

Zinc oxide (ZnO) crystals have recently drawn attention due to a relatively low price and to their application perspectives in various fields [1]. Commercially available crystals and substrates are usually obtained by hydrothermal methods [1,2]. However, the corresponding equipment is very expensive, and the presence of mobile Li or K ions in these materials usually limits their utilization in electronics [1]. Only the special adjustments of critical growth conditions provided recently the decrease in concentration of these impurities down to 10^{14} cm^{-3} [3].

The recent viable direction of wide band-gap II–VI semiconductor compounds application is the fabrication of nanoporous matrices (NM) (nanotemplates), which give the possibility of obtaining nanowires and nanotubes of various materials as promising structures for optoelectronics and photonics. The easiest and most cost-effective method to obtain NM is electro-chemical etching (ECE), which, however, can be efficiently used only on the homogeneously doped substrates with controllable high conductive properties [4–6]. The increase in the substrate conductivity provides the decrease in the diameter of pores.

In this regard, great interest is the elaboration of cheap and simpler growth methods of ZnO single crystals with controllable electrical parameters and impurity composition varied in a wide range. One of the most suitable methods for obtaining such crystals is the chemical vapor transport (CVT) in sealed chambers.

The use of H_2 as a chemical vapor transport agent (TA) gives the possibility to grow large ZnO crystals with the growth rate of up to 2 mm per day. However, these crystals are usually characterized by structural defects such as angle boundaries and voids [7,8]. Furthermore, a strong mechanical contact between crystals and walls of quartz growth chambers leads to a partial destruction of crystals during a post-growth cooling. Using HI and HBr as a TA has not allowed reaching the high growth rate of bulk crystals [9]. The application of chloride compounds as a TA, which effectively react with ZnO and can provide a dense medium of chemical interaction products, might be a perspective. Moreover, it can be also the perspective for obtaining materials homogeneously doped by various metal chlorides in the growth process, as well as solid solution crystals based on ZnO, as it was recently demonstrated for obtaining ZnCdS:HCl single crystals [6]. The use of HCl or $ZnCl_2 + H_2O$ vapor mixtures as TAs in open CVT systems is effective for obtaining ZnO epitaxial layers and nanowalls [10–12]. Nevertheless, it was reported that the utilization of NH_4Cl, Cl_2, $HgCl_2$

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